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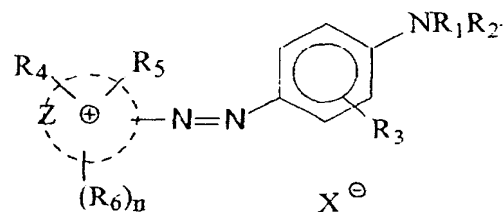
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(54) **Ink jet printing method**

(57) An ink jet printing method, comprising the steps of:

- A) providing an ink jet printer that is responsive to digital data signals;
 B) loading said printer with ink-receptive elements comprising a support having thereon a porous ink-receptive layer;
 C) loading said printer with an ink jet ink composition comprising water, a humectant, and a water-dispersible polymeric latex having contained therein a delocalized cationic azo dye derived from the quaternization of a nitrogen heterocyclic azo dye having the following formula:



- and
 D) printing on an ink-receptive substrate using said ink jet ink in response to said digital data signals.

Description

[0001] This invention relates to an ink jet printing method using an ink jet ink composition containing cationic dyes and a polymer latex.

[0002] Ink jet printing is a non-impact method for producing images by the deposition of ink droplets in a pixel-by-pixel manner to an image-recording element in response to digital signals. There are various methods which may be utilized to control the deposition of ink droplets on the image-recording element to yield the desired image. In one process, known as continuous ink jet, a continuous stream of droplets is charged and deflected in an imagewise manner onto the surface of the image-recording element, while unimaged droplets are caught and returned to an ink sump. In another process, known as drop-on-demand ink jet, individual ink droplets are projected as needed onto the image-recording element to form the desired image. Common methods of controlling the projection of ink droplets in drop-on-demand printing include piezoelectric transducers and thermal bubble formation. Ink jet printers have found broad applications across markets ranging from industrial labeling to short run printing to desktop document and pictorial imaging.

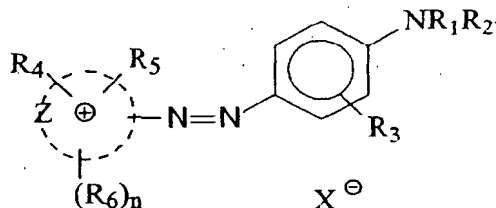
[0003] Commercial dye based inks are commonly composed of a chromophoric unit which has attached to it, by some means, an anionic functionality. The receiver material commonly possesses some kind of cationic functionality, so that the integrity of the image is maintained by means of a salt type link, between the dye and receiver material as described in EP 970819A2. Much less common is the reverse of this system where the dye is cationic and the receiver contains the anionic function as described in EP1010539A1. There are always limitations for the above two scenarios that the right dye-mordant combination has to be chosen in order to obtain high quality ink jet prints with good water-fastness and light fastness.

[0004] U.S. Patent 5,560,996 discloses a variety of cationic dyes, including cationic azo dyes such as Basic Red 46 and other cationic magenta dyes such as Basic Reds 12, 14 and 15 for use in an ink jet ink. However, there is a problem with these dyes in that they have poor light stability.

[0005] It is an object of this invention to provide an ink jet printing method using an ink composition that is capable of yielding print images with consistent light fastness irrespective of the receiver type.

[0006] This and other objects are achieved in accordance with this invention which relates to an ink jet printing method, comprising the steps of:

- A) providing an ink jet printer that is responsive to digital data signals;
- B) loading the printer with ink-receptive elements comprising a support having thereon a porous ink-receptive layer;
- C) loading the printer with an ink jet ink composition comprising water, a humectant, and a water-dispersible polymeric latex having contained therein a delocalized cationic azo dye derived from the quaternization of a nitrogen heterocyclic azo dye having the following formula:



wherein:

Z represents the atoms necessary to complete a nitrogen-containing heterocyclic ring containing 2 or 3 nitrogen atoms and the balance carbon atoms;

R₁ and R₂ each independently represents hydrogen or a substituted or unsubstituted alkyl group of 1 to 6 carbon atoms;

R₄, R₅ and R₆ each independently represents the same substituents as R₁ and R₂, halogen, cyano, substituted or unsubstituted alkoxy, acyl, benzoyl or alkoxycarbonyl; with the proviso that at least one of R₄, R₅ and R₆ represents a substituted or unsubstituted alkyl group of 1 to 6 carbon atoms attached to a nitrogen atom;

R₃ represents the same groups as R₄, R₅ and R₆; hydroxy; a polyoxyalkylene group of 2-20 alkylene oxide residues; carboxy or sulfo or phospho ester; carbamoyl; substituted or unsubstituted alkyl-, aryl-, aralkyl-, diaryl- or dialkyl-carbamoyl of 1 to 20 carbon atoms; sulfamoyl; substituted or unsubstituted alkyl-, aryl-, aralkyl-, diaryl- or dialkyl-sulfamoyl of 1 to 20 carbon atoms; acylamino; sulfonylamino; amino; a substituted or unsub-

stituted alkyl-, aryl-, aralkyl-, diaryl- or dialkylamino- of 1 to 20 carbon atoms; or a quaternary ammonium or phosphonium group; or may be combined with R_2 to form a carbocyclic or heterocyclic 5 or 6 membered ring; n is 1 except when Z represents the atoms necessary to complete a nitrogen-containing heterocyclic ring containing 3 nitrogen atoms, in which case n is 0; and

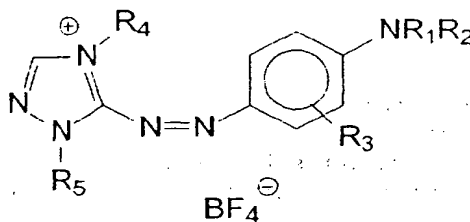
X represents a counterion, such as citrate, gluconate or lactate; with the proviso that when Z represents the atoms necessary to complete a nitrogen-containing heterocyclic ring of 3 nitrogen atoms, then R_3 is combined with R_2 to form a carbocyclic or heterocyclic 5 or 6 membered ring; and

D) printing on an ink-receptive substrate using the ink jet ink in response to the digital data signals.

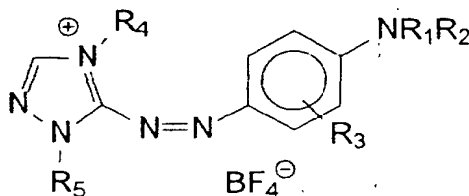
[0007] It has been found that use of the above dyes provide excellent light stability for the printed image on a variety of different ink jet receivers when a water dispersible polymer latex is contained in the ink composition irrespective of the receiver type.

[0008] Quaternized nitrogen heterocyclic-azo dyes are not new. They have been used for dyeing fabrics, particularly polyacrylonitrile fabrics. Typical examples are quaternized pyrazole-azo, imidazole-azo, triazole-azo dyes. Their use has been described for this purpose in "Chemistry and Application of Dyes" ed D.R. Waring and G. Hallas, (Plenum Press), p184. A typical preparation of dyes of this type is also described in the above reference (p197).

[0009] Representative examples of dyes employed in the invention are:



Dye	R_1	R_2 - R_3	R_4	R_5	λ -max (nm)
1	n-C ₄ H ₉	2,2,4,7-Tetramethyl tetrahydroquinoline	CH ₃	CH ₃	547
2	-H	2,2,4,7-Tetramethyl tetrahydroquinoline	CH ₃	CH ₃	534
3	n-C ₄ H ₉	2,2,4,7-Tetramethyl tetrahydroquinoline	C ₂ H ₅	C ₂ H ₅	549
4	C ₂ H ₅	2-Methylbenzoxazine	CH ₃	CH ₃	546
5	C ₂ H ₄ OH	2,2,4-Trimethyl tetrahydroquinoline	CH ₃	CH ₃	544



Dye	R_1	R_2	R_3	R_4	R_5	R_6	λ max
6	n-C ₄ H ₉	2,2,4,7-Tetramethyl tetrahydroquinoline		CH ₃	CH ₃	CONH(C ₂ H ₄ OH) ₂	551
7	C ₂ H ₄ Cl	2,2,4,7-Tetramethyl tetrahydroquinoline		CH ₃	CH ₃	CO ₂ CH ₃	530
8	C ₂ H ₅	2,2,4-Trimethyl tetrahydroquinoline		CH ₃	CH ₃	CONHC ₄ H ₉	550
9	C ₂ H ₅	C ₂ H ₅	H	CH ₃	CH ₃	CN	550

(continued)

Dye	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	λ max
10	n-C ₄ H ₉	2,2,4,7-Tetramethyl tetrahydroquinoline		CH ₃	CH ₃	CO ₂ CH ₃	546
11	n-C ₃ H ₇	n-C ₃ H ₇	3-NHCOCH ₃	CH ₃	CH ₃	CO ₂ CH ₃	544
12	C ₂ H ₅	C ₂ H ₅	3-CH ₃	CH ₃	CH ₃	CN	554

[0010] In a preferred embodiment of the invention, R₁ in the above formula represents hydrogen. In another preferred embodiment, R₂ represents C₄H₉. In still another preferred embodiment, R₂ and R₃ are taken together and represent a tetrahydroquinoline ring. In yet another preferred embodiment, R₄ represents CN or CON(C₂H₄OH)₂. In still another preferred embodiment, R₅ and R₆ each represents CH₃.

[0011] In general, the above dyes comprise from 0.2 to 5%, preferably from 0.5 to 3%, by weight of the ink jet composition.

[0012] The cationic dyes employed in the present invention should be practically water insoluble, with the solubility in water preferably less than 0.1 g/l at 25 °C, and the solubility in organic solvents such as methanol, acetone, ethyl acetate and tetrahydrofuran greater than or equal to 0.2 g/l. The solubility of the counterion X⁻. The counterions preferred for solubility are BF₄⁻, OTs⁻, PF₆⁻, C₁₂H₂₅SO₃⁻ and ClO₄⁻.

[0013] The dye-containing polymeric latex employed in the invention can be prepared by dissolving the dye in a water-miscible organic solvent, mixing the solution with the latex and then removing the solvent. Useful water-miscible organic solvents are water-miscible alcohols, ketones and amides, tetrahydrofuran, N-methyl-2-pyrrolidone, dimethylsulfoxide and mixtures thereof, such as acetone, ethyl alcohol, methyl alcohol, isopropyl alcohol, dimethylformamide, methyl-ethyl ketone etc.

[0014] The ink jet ink containing the water-dispersible polymeric latex employed in the invention consists of water as a continuous phase and dye-containing polymeric latex as a dispersed phase. In a preferred embodiment of the invention, the polymeric latex meets the following test: At 25° C., the polymeric latex must: (a) be capable of forming a stable dispersion with water at a concentration of from 0.2 to 50 percent by weight, preferably 1 to 20 percent by weight, and (b) when 100 ml of the latex is then mixed in an equal volume of the water-miscible organic solvent described above, stirred and allowed to stand for 10 minutes, exhibit no observable coagulation of the polymeric latex. In order to be useful in the ink, the latex should have an average particle size of < 1 μm, preferably < 0.5 μm.

[0015] Aqueous lattices can be prepared by free radical polymerization or by condensation polymerization. Emulsion polymerization is the preferred method of preparing polymer lattices. Monomers suitable to prepare the polymer lattices for this application include an acrylic acid, for example, acrylic acid, α-chloroacrylic acid, an α-alkylacrylic acid (such as methacrylic acid, etc.), etc., an ester or amide derived from an acrylic acid (for example, acrylamide, methacrylamide, n-butylacrylamide, 1-butylacrylamide, diacetone acrylamide, methyl acrylate, ethyl acrylate, n-propyl acrylate, n-butyl acrylate, tert-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, lauryl acrylate, tetrahydrofuryl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, β-hydroxy methacrylate, tetrahydrofuryl methacrylate, etc.), a vinyl ester (for example, vinyl acetate, vinyl propionate, vinyl laurate, etc.), acrylonitrile, methacrylonitrile, an aromatic vinyl compound (for example, styrene and a derivative thereof, vinyl toluene, divinyl benzene, vinyl acetophenone, sulfostyrene, etc.), itaconic acid, citraconic acid, crotonic acid, vinylidene chloride, a vinyl alkyl ether (for example, vinyl ethyl ether, etc.), an ester of maleic acid, N-vinyl-2-pyrrolidone, N-vinylpyridine, 2- or 4-vinylpyridine, etc. Of these monomers, an ester of acrylic acid, an ester of methacrylic acid, and styrene and styrene derivatives are particularly preferred. Two or more ethylenic unsaturated monomers can be used together. For example, a combination of methyl acrylate and butyl acrylate, ethyl acrylate and styrene, tetrahydrofuryl methacrylate and ethylacrylate, methyl acrylate and ethyl acrylate, etc., can be used.

[0016] The polymeric latex used in the invention can be prepared by emulsion polymerization or solution polymerization technique. Emulsion polymerization is preferred. Emulsion polymerization is well known in the art and is described, for example, in F. A. Bovey, Emulsion Polymerization, issued by Interscience Publishers Inc. New York, 1955. Examples of the chemical initiators which may be used include a thermally decomposable initiator, for example, a persulfate (such as ammonium persulfate, potassium persulfate, sodium persulfate), hydrogen peroxide, 4,4'-azobis (4-cyanovaleric acid), and redox initiators such as hydrogen peroxide-iron(II) salt, potassium persulfate-sodium hydrogensulfate, potassium persulfate-sodium metabisulfite, potassium persulfate-sodium hydrogen bisulfite, cerium salt-alcohol, etc. Emulsifiers which may be used in the emulsion polymerization include soap, a sulfonate (for example, sodium N-methyl-N-oleoyltaurate, sodium dodecylbenzene sulfonate, α-olefin sulfonate, diphenyloxide disulfonate, naphthalene sulfonate, sulfosuccinates and sulfosuccinamates, polyether sulfonate, alkyl polyether sulfonate, alkylaryl polyether sulfonate, etc.), a sulfate (for example, sodium dodecyl sulfate), a phosphate (for example, nonylphenol ethoxylate phosphate, linear alcohol alkoxyate phosphate, alkylphenol ethoxylate phosphate, phenol ethoxylate), a

cationic compound (for example, cetyl trimethylammonium bromide, hexadecyl trimethylammonium bromide, etc.), an amphoteric compound and a high molecular weight protective colloid (for example, polyvinyl alcohol, polyacrylic acid, gelatin, etc.).

[0017] A second class of polymeric lattices used in the invention may be an aqueous dispersible polyester such as Eastman AQ® polyesters produced by the Eastman Chemical Company. The three polyesters, Eastman AQ 29®, AQ 38®, and AQ 55® are composed of varying amounts of isophthalic acid, sodium sulfoisophthalic acid, diethylene glycol, and 1,4-cyclohexanedimethanol. These thermoplastic, amorphous, ionic polyesters are prepared by a melt-phase condensation polymerization at high temperature and low pressure, and the molten product is extruded into small pellets. The solid polymer disperses readily in water at 70°C with minimal agitation to give translucent, low viscosity dispersions containing no added surfactants or solvents. Varying the amount of ionic monomers, i.e., sulfoisophthalic acid, can control the particle size. The particle sizes range from 20 to 100nm.

[0018] A third class of polymeric lattices used in the invention may be an aqueous dispersible polyurethane such as Witcobond® anionic and cationic polyurethane dispersion by Witco Corp. or Sancure® polyurethane by BF Goodrich Company.

[0019] In addition to the colorant, other ingredients are also commonly added to ink jet inks. Water miscible organic solvents humectants and/or co-solvents may be added to aqueous inks to help prevent the ink from drying out or crusting in the orifices of the printhead or to help the ink penetrate the receiving substrate, especially when the substrate is a highly sized paper. Examples of such solvents include glycols and derivatives thereof, including propylene glycol, polypropylene glycol, ethylene glycol, polyethylene glycol, diethylene glycol, glycerol, thiodiethanol, tetraethylene glycol (and mixtures and derivatives thereof), low molecular weight alcohols such as ethanol and isopropanol and amides such as N-methylpyrrolidone.

[0020] A humectant is employed in the ink jet composition employed in the invention to help prevent the ink from drying out or crusting in the orifices of the printhead. Examples of humectants which can be used include polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, 2-methyl-2,4-pentanediol, 1,2,6-hexanetriol and thioglycol; lower alkyl mono- or di-ethers derived from alkylene glycols, such as ethylene glycol mono-methyl or mono-ethyl ether, diethylene glycol mono-methyl or mono-ethyl ether, propylene glycol mono-methyl or mono-ethyl ether, triethylene glycol mono-methyl or mono-ethyl ether, diethylene glycol di-methyl or di-ethyl ether, and diethylene glycol monobutylether; nitrogen-containing cyclic compounds, such as pyrrolidone, N-methyl-2-pyrrolidone, and 1,3-dimethyl-2-imidazolidinone; and sulfur-containing compounds such as dimethyl sulfoxide and tetramethylene sulfone. A preferred humectant for the composition used in the invention is diethylene glycol, glycerol, or diethylene glycol monobutylether.

[0021] Water-miscible organic solvents may also be added to the aqueous ink employed in the invention to help the ink penetrate the receiving substrate, especially when the substrate is a highly sized paper. Examples of such solvents include alcohols, such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, iso-butyl alcohol, furfuryl alcohol, and tetrahydrofurfuryl alcohol; ketones or ketoalcohols such as acetone, methyl ethyl ketone and diacetone alcohol; ethers, such as tetrahydrofuran and dioxane; and esters, such as, ethyl lactate, ethylene carbonate and propylene carbonate.

[0022] Surfactants may be added to adjust the surface tension of the ink to an appropriate level. The surfactants may be anionic, cationic, amphoteric or nonionic.

[0023] A biocide may be added to the composition employed in the invention to suppress the growth of micro-organisms such as molds, fungi, etc. in aqueous inks. A preferred biocide for the ink composition of the present invention is Proxel® GXL (Zeneca Specialties Co.) at a final concentration of 0.0001-0.5 wt. %.

[0024] The pH of the aqueous ink compositions employed in the invention may be adjusted by the addition of organic or inorganic acids or bases. Useful inks may have a preferred pH of from 2 to 10, depending upon the type of dye being used. Typical inorganic acids include hydrochloric, phosphoric and sulfuric acids. Typical organic acids include methanesulfonic, acetic and lactic acids. Typical inorganic bases include alkali metal hydroxides and carbonates. Typical organic bases include ammonia, triethanolamine and tetramethylethylenediamine.

[0025] A typical ink composition employed in the invention may comprise, for example, the following substituents by weight: colorant (0.05-5%), water (20-95%), a humectant (5-70%), water miscible co-solvents (2-20%), surfactant (0.1-10%), biocide (0.05-5%) and pH control agents (0.1-10%).

[0026] Additional additives which may optionally be present in the ink jet ink composition employed in the invention include thickeners, conductivity enhancing agents, anti-kogation agents, drying agents, and defoamers.

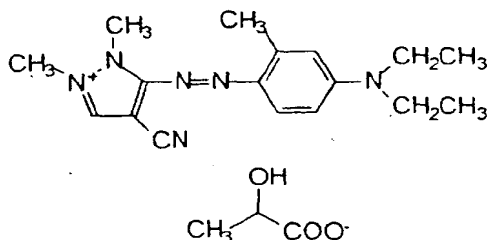
[0027] The ink jet inks employed in this invention may be employed in ink jet printing wherein liquid ink drops are applied in a controlled fashion to an ink receptive layer substrate, by ejecting ink droplets from a plurality of nozzles or orifices of the print head of an ink jet printer.

[0028] Ink-receptive substrates useful in ink jet printing are well known to those skilled in the art. Representative examples of such substrates are disclosed in U.S. Patents 5,605,750; 5,723,211; and 5,789,070 and EP 813 978 A1.

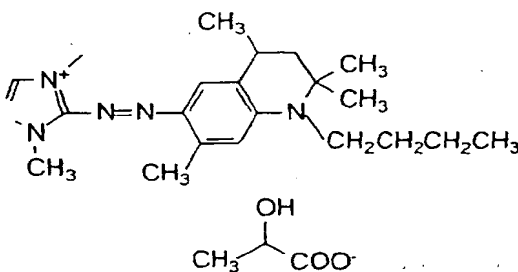
[0029] The following examples illustrate the utility of the present invention.

Control Ink C-1 (no polymer latex)

[0030] To prepare the comparative ink jet ink, 4.07 g of the aqueous stock solution (2.5% by weight) of water soluble dye Control 1 (below), 0.075 g Surfynol® 465 (from Air Products), 0.9 g glycerol, 0.9 g diethylene glycol were added to 9.06 g distilled water. The final ink contained 0.68 % dye, and 0.5 % Surfynol® 465, 6 % glycerol, 6 % diethylene glycol. The solution was filtered through a 0.45 µm polytetrafluoroethylene filter and filled into a refillable ink jet cartridge.

Control 1Control Ink C-2 (no polymer latex)

[0031] This composition was prepared similar to C-1 except that 3.78 g of the aqueous stock solution (4 % by weight) of water soluble dye Control 2 (below) was used instead of Control 1. The final ink contained 1.0 % dye.

Control 2Ink 1 (Contains latex-Invention)

[0032] To 4.8 g of 31.2% commercially available latex dispersion AQ55® (from Eastman Chemical Co.) was added 10.2 g of water and 15.0 g of methanol to form a diluted polymer dispersion. A solution of dye 1 (above) in methanol (300 mg in 25 ml of methanol) was added dropwise to the above AQ55® dispersion with continuous stirring. After 1 hour, the organic solvent was removed under reduced pressure. The resulting stock solution was filtered through a 0.45 µm filter. The concentration of dye 1 in the latex stock solution was estimated to be 2.0%, and the polymer concentration was ~10% by weight.

[0033] To prepare the ink solution, 7.5 g of the above latex solution, 0.075 g Surfynol® 465 (from Air Products), 0.9 g glycerol and 0.9 g diethylene glycol were added to 5.62 g distilled water.

Ink 2 (Contains latex-Invention)

[0034] A composition similar to Ink 1 was prepared except that Dye 12 was used instead of Dye 1. To prepare the AQ55® latex containing Dye 12, 210 mg of Dye 12 was dissolved in 20 ml of methanol.

Stability Tests

Table

Claims

Z represents the atoms necessary to complete a nitrogen-containing heterocyclic ring containing 2 or 3 nitrogen atoms and the balance carbon atoms;

R₁ and R₂ each independently represents hydrogen or a substituted or unsubstituted alkyl group of 1 to 6 carbon atoms;

R₄, R₅ and R₆ each independently represents the same substituents as R₁ and R₂; halogen, cyano, substituted or unsubstituted alkoxy, acyl, benzoyl or alkoxycarbonyl; with the proviso that at least one of R₄, R₅ and R₆ represents a substituted or unsubstituted alkyl group of 1 to 6 carbon atoms attached to a nitrogen atom;

R₃ represents the same groups as R₄, R₅ and R₆; hydroxy; a polyoxyalkylene group of 2-20 alkylene oxide residues; carboxy or sulfo or phospho ester, carbamoyl; substituted or unsubstituted alkyl-, aryl-aralkyl-, diaryl- or dialkyl-carbamoyl of 1 to 20 carbon atoms; sulfamoyl; substituted or unsubstituted alkyl-, aryl-, aralkyl-, diaryl- or dialkyl-sulfamoyl of 1 to 20 carbon atoms; acylamino; sulfonylamino; amino; a substituted or unsubstituted alkyl-, aryl-, aralkyl-, diaryl- or dialkylamino- of 1 to 20 carbon atoms; or a quaternary ammonium or phosphonium group; or may be combined with R₂ to form a carbocyclic or heterocyclic 5 or 6 membered ring;

n is 1 except when Z represents the atoms necessary to complete a nitrogen-containing heterocyclic ring containing 3 nitrogen atoms, in which case n is 0; and

X represents a counterion;

with the proviso that when Z represents the atoms necessary to complete a nitrogen-containing heterocyclic ring of 3 nitrogen atoms, then R₃ is combined with R₂ to form a carbocyclic or heterocyclic 5 or 6 membered ring; and

D) printing on an ink-receptive substrate using said ink jet ink in response to said digital data signals.

2. The method of Claim 1 wherein R₁ in the above formula represents hydrogen.
3. The method of Claim 1 wherein R₂ represents C₄H₉.
4. The method of Claim 1 wherein R₂ and R₃ are taken together and represent a tetrahydroquinoline ring.
5. The method of Claim 1 wherein R₄ represents CN.
6. The method of Claim 1 wherein X⁻ represents BF₄⁻, OTs⁻, PF₆⁻, C₁₂H₂₅SO₃⁻ and ClO₄⁻.
7. The method of Claim 1 wherein R₅ and R₆ each represents CH₃.
8. The method of Claim 1 wherein R₄ represents CON(C₂H₄OH)₂.
9. The method of Claim 1 wherein said dye comprises 0.2 to 5 % by weight of said ink jet ink composition.
10. The method of Claim 1 wherein said water-dispersible polymeric latex comprises a polyester, a polyurethane or an acrylate.